Investigation of a PbSCC of an Alloy 600 SG Tube at a High Temperature using an Electrochemical Noise Technique

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1. Introduction

Since a fluctuation of the electrochemical potential and current associated with such localized corrosions as a pitting, crevice corrosion and stress corrosion cracking (SCC) have been observed in experimental data, an electrochemical noise (EN) measurement has become a useful technique for monitoring these localized corrosions [1, 2]. Moreover, it has also been reported that this technique is powerful enough to distinguish between different types of localized corrosions based on a stochastic theory using a probability of the EN parameters such as the frequency of events, the noise resistance, the average charge of events [1] and the mean free time to failure [2]. In this respect, the present work is aimed at applying the EN technique to investigate a Pb-induced SCC of an Alloy 600 steam generator (SG) tubing in a pressurized water reactor (PWR) based on the stochastic theory.

2. Experimental

EN measurement was carried out with a Zahner IM6e equipped with a Zahner NProbe. Two Alloy 600 C-ring specimens were galvanically coupled using the zero-resistance ammeter (ZRA) mode of IM6e. These C-ring were manufactured from an Alloy 600 SG tubing as low temperature mill-annealed (LTMA) with an outer diameter of 22.23 mm and a thickness of 1.27 mm according to ASTM G38. One was stressed to 150% of its room temperature YS at the apex with an Alloy 600 bolt and nut, and the other was unstressed. The reference electrode was an external Ag/AgCl electrode filled with a 0.1 M KCl solution (Toshin-Kogyo Co.).

Electrochemical potential noise (EPN) and current noise (ECN) of the specimens were recorded first in a 40 wt% NaOH solution containing 10,000 ppm PbO for 264 hrs at 290 ^{o}C. After that, 200 ppm CuO was added to the solution and the corrosion potential of the stressed specimen was recorded for 14 hrs at 290 ^{o}C with the EN monitoring, and then a further 300 ppm CuO was added to the solution to verify the change in the corrosion potential with the addition of CuO. The specimens were immersed in the solution containing both PbO and CuO for 136 hrs in total at 290 ^{o}C. After an entire immersion test, the specimens were chemically etched with a solution of 2% bromine + 98% methanol, and then they were examined by a scanning electron microscopy (SEM, JEOL JSM-6360) equipped with an energy dispersive spectrometer (EDS, Oxford-7582).

3. Results and Discussion

3.1 Microscopic analysis

After the immersion test in the caustic solution containing PbO for 264 hrs at 290 ^{o}C, a local break-down of the surface film was frequently observed on the specimen surface, but the crack in the surface film did not seem to be propagated into the Alloy 600 matrix yet. After an entire immersion test in the solution containing both PbO and CuO at 290 ^{o}C, several cracks were propagated. From SEM analysis of the C-ring specimen after an entire immersion test, it was found that the crack was propagated in an intergranular (IG) mode and the crack mouth and tip were covered by a surface film. From the analysis of the chemical composition of the surface film with EDS, Pb was detected at the oxide film of both the crack mouth and tip. These are typical of a PbSCC of Alloy 600 in a caustic solution [3].

3.2 Electrochemical noise analysis

Figs. 1(a) and (b) present the typical EPN and ECN recorded for the solution containing PbO for the time period from 720,000 to 770,000 s, and for the solution containing both PbO and CuO for the time period from 1,330,000 to 1,436,000 s, respectively. There were typical potential drops in the EPN with simultaneous current rises in the ECN, which have generally been observed during localized corrosions such as the pitting, crevice corrosion, intergranular corrosion and SCC [1]. The current transient accompanied by a random potential drop in Fig. 1(a) revealed a repetitive increase and decrease in a stepwise manner of a lower amplitude and of a shorter time interval when compared to the current transient exhibiting a rapid rise and a slow fall in Fig. 1(b).

Based on a shot-noise theory [1], the frequency of events f_n of the localized corrosions is estimated for each time record as given by,

$$f_n = B^2/(\Psi_E A) \quad (1),$$

where B is the Stern-Geary coefficient, Ψ_E the PSD value of the EPN obtained by averaging several of the low-frequency points using the FFT algorithm and A

represents the exposed electrode area. From a set of f_n calculated from the PSD plots according to Eq. (1), the cumulative probability $F(f_n)$ at each f_n is determined numerically by a mean rank approximation [1]. In this work, to understand the stochastic characteristics of PbSCC, the probability of f_n was analyzed using the Weibull distribution function [2] which is one of the most commonly used cumulative probability functions for predicting a life and failure rate expressed as,

$$\ln\{\ln[1/(1-F(t))]\} = m \ln t - \ln n \qquad (2),$$

where t is the mean free time which corresponds to $1/f_n$, and m and n represent the shape and scale parameters, respectively.

Fig. 2 depicts the plots of $\ln\{\ln[1/(1-F(t))]\}$ vs. ln t determined numerically from the sets of f_n by the mean rank approximation which were calculated from the PSD plots in the same time period of Fig. 1. In Fig. 2, the shift of the mean free time t to a higher value, that is, the shift of f_n to a lower frequency, was found in the time period at which the decrease of the EPN with simultaneous decrease of the ECN was detected from the stressed specimens in the caustic solution with additives, as compared to that obtained from the unstressed specimen in the caustic solution without additives where only the uniform corrosion is expected to occur. This also means that there were localized corrosion events occurring at the stressed specimens.

In the case of the plot obtained from the unstressed Alloy 600 specimen in the caustic solution without impurities, the value of m is estimated as 1.67. However, the value of m is determined as 0.59 and 0.17 for the stressed specimen in the solution containing PbO and in the solution containing both PbO and CuO, respectively, from the mean free time period where the probability deviates considerably from that of the unstressed Alloy 600 specimen as shown in Fig. 2. From the comparison between the microscopic and electrochemical noise analysis, the value of m determined from the stressed specimen in the solution containing PbO can be regarded as a kinetic parameter mainly related with the initiation of PbSCC consisting of such stochastic processes as the local break-down and repassivation of the surface oxide film, and that value estimated in the solution containing both PbO and CuO can be assumed to be the kinetic parameter closely related with the propagation of PbSCC.

4. Conclusion

From the analysis of the EN obtained from the Alloy 600 SG tube materials in the simulated caustic solution environment of SG sludge piles at a high temperature, it is strongly suggested that the random potential drop with a shorter time interval accompanied by a repetitive current increase with a lower amplitude in a stepwise manner is attributable to the initiation of a PbSCC composed of a local break-down and repassivation of a surface oxide film, whereas the potential drop with a longer time interval accompanied by a current increase with a larger amplitude is mainly due to the propagation of a PbSCC.

REFERENCES

[1] R.A. Cottis, Corrosion 57 (2001) 265.
[2] K.H. Na, S.I. Pyun, H.P. Kim, J. Electrochem. Soc. 154 (2007) C349.
[3] S.S. Hwang, H.P. Kim, D.H. Lee, U.C. Kim, J.S. Kim, J. Nucl. Mater. 275 (1999) 28.

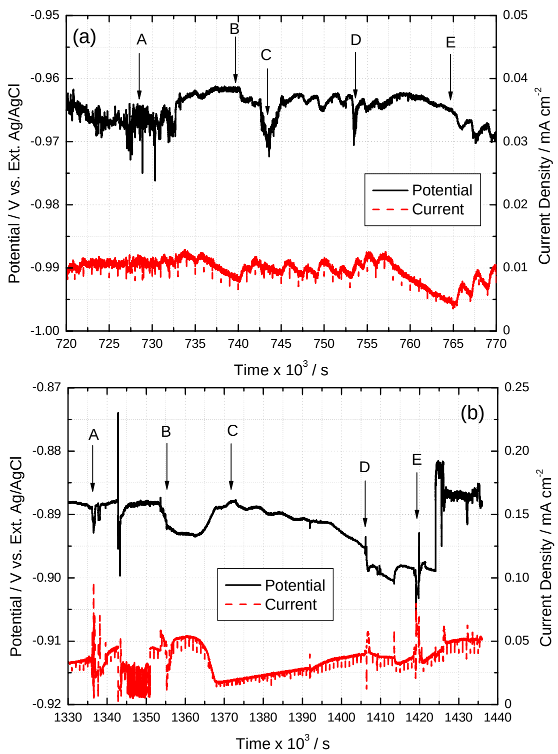

Fig. 1. Time records of the EPN and ECN measured from the stressed C-ring specimens (a) in the solution containing PbO from 720,000 to 770,000 s, and (b) in the solution containing both PbO and CuO from 1,330,000 to 1,436,000 s, respectively.

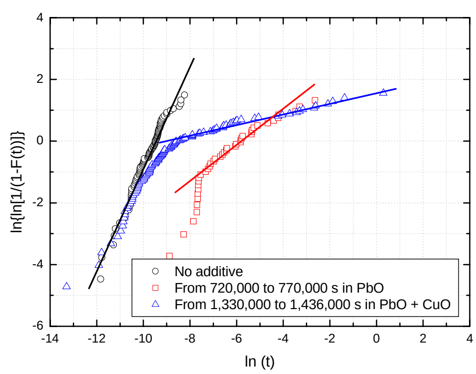

Fig. 2. Plots of $\ln\{\ln[1/(1-F(t))]\}$ vs. ln t determined using the sets of fn for the stressed C-ring specimens in the same time region of Fig. 1. The plot obtained for unstressed wire specimen in a 40 wt% NaOH solution without impurities at 290 ^{o}C is also given in figure.